

Influence of Deacetylation on the Rheological Properties of Xanthan–Guar Interactions in Dilute Aqueous Solutions

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ABSTRACT: An oscillating capillary rheometer was used to investigate the effects of xanthan deacetylation on the viscoelastic properties and intrinsic viscosity of xanthan and guar mixtures in dilute aqueous solutions. Deacetylated xanthan exhibited a stronger synergistic interaction with guar than native xanthan did due to the destabilized helical structure and increased chain flexibility of the deacetylated xanthan. No gels were observed for all xanthan–guar mixtures. Native xanthan–guar mixtures exhibited a liquid-like behavior, whereas deacetylated xanthan–guar mixtures exhibited a gel-like behavior. The relative viscosity and elasticity of deacetylated xanthan–guar mixtures were much stronger than those for native xanthan–guar mixtures. The intrinsic viscosities of deacetylated xanthan–guar mixtures were higher than the calculated values assuming no interaction, whereas the intrinsic viscosities of native xanthan–guar mixtures were lower than the calculated values assuming no interaction, demonstrating that intermolecular binding occurred between the disordered segments of xanthan and guar gum in dilute aqueous solutions.

Keywords: deacetylation, dilute solutions, intrinsic viscosity, viscoelastic properties, xanthan–guar mixtures

Introduction

Xanthan gum is an anionic heteropolysaccharide produced by the microorganism *Xanthomonas campestris*. Xanthan's main backbone consists of (1→4) β -D-glucopyranosyl units substituted at C-3 on every other glucose residue with a charged trisaccharide sidechain (Jansson and others 1975). The trisaccharide chain consists of a D-glucuronic acid unit between 2 D-mannose units. Approximately one-half of the terminal D-mannose unit contains a pyruvic acid residue linked via keto groups to the four and six positions, with an unknown distribution. The D-mannose linked to the main chain contains an acetyl group at position O-6 (Garcia-Ochoa and others 2000). The acetate and pyruvate contents are variable on the side chain, and depend on the bacterial strains and on the fermentation conditions used to produce the gum. In aqueous solutions, the secondary structure of xanthan undergoes an "order–disorder" transition from helix to coil structure. This conformational transition depends on temperature, ionic strength of solutions, nature of electrolyte, pH, and acetyl and pyruvate constituent contents (Holzwarth 1976; Morris and others 1977; Baradossi and Brant 1982; Paoletti and others 1983; Norton and others 1984).

Guar gum is obtained from the seed of the guar plant, *Cyanopsis tetragonolobus*, and has the general structure of galactomannans. Guar consists of a main chain (1→4) β -D-mannopyranosyl unit substituted at O-6 by single-unit side-chains of α -D-galactopyranose. The ratio of mannose to galactose is approximately 1.6:1, depending on the source and method of extraction used to isolate the gum (Dea and Morrison 1975).

Synergistic polysaccharide–polysaccharide interactions are attractive in the food industry because they impart novel and improved texture and rheological characteristics to food products, and they reduce polymer costs (Williams and Phillips 2000). Many researchers have observed synergistic interaction between xanthan gum and galactomannans in solutions that resulted in enhanced viscosity or gelation (Rocks 1971; Dea and Morrison 1975; Dea and others 1977; Morris and others 1977). Although a few researchers (Kovacs 1973; Doublier and Llamas 1991; Schorsch and others 1995) have invoked the concept of mutual incompatibility to explain the interaction mechanism between xanthan and galactomannans, there is increasing evidence that supports intermolecular binding between xanthan and galactomannans (Dea and others 1977; Morris and others 1977; McCleary 1979; Tako and others 1984; Cairns and others 1986, 1987; Cheetham and others 1986; Cheetham and Mashimba 1988, 1991; Tako 1991; Mannion and others 1992; Zhan and others 1993; Khouryieh and others 2006).

To date, the intermolecular binding mechanism between xanthan and galactomannans is still controversial, and different models have been proposed. The first model was proposed by Morris and others (1977) and Dea and others (1977), who suggested the intermolecular binding concept rather than mutual exclusion to explain the gelation mechanism between xanthan and galactomannans. The authors proposed that the synergistic interaction between xanthan and galactomannan is based on a cooperative interaction, depending on the fine structure of the galactomannan. The intermolecular binding involves binding of unsubstituted regions of the galactomannan to the ordered xanthan helical structure. McCleary (1979) modified the above model in order to explain the strong interaction between xanthan and certain high-galactose galactomannans. They suggested that the interaction involve the ordered xanthan and sequences along the mannan backbone where the galactosyl units are located on one side only.

The 2nd model was proposed by Cairns and others (1986, 1987) in which intermolecular binding occurred between the disordered

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xanthan and galactomannans, and disordering of xanthan helical structure is necessary for gelation. They proposed that xanthan has a disordered, extended, 2-fold, cellulose-like conformation, rather than a 5-fold helix, when interacting with galactomannan. Cheetham and others (1986) and Cheetham and Mashimba (1988, 1991) proposed that the interaction occurs between the disordered segments of the xanthan chains and galactomannan.

The 3rd model was proposed by Tako and others (1984), Tako and Nakamura (1985), and Tako (1991) in which the intermolecular binding occurs between the side chains of xanthan in the helical form and backbone of the galactomannans. They suggested that the side chains of the xanthan are inserted into adjacent unsubstituted regions of the galactomannan backbone, which adopted an extended, 2-fold, ribbon-like conformation.

Shatwell and others (1991) conducted rheological and chiroptical studies on a range of xanthan with various amounts of acetyl and pyruvic acid substitution. Oscillatory-shear measurements were determined upon mixed systems consisting of 0.5% (w/w) xanthan and 1.0% (w/w) guar gum in deionized water. The enhanced viscosity of xanthan–guar mixture was due solely to the presence of topological entanglements and not to a more specific intermolecular interaction. Evidence from both rheological and chiroptical results indicated a possible weak interaction between some low-acetyl xanthans and guar, but the nature of this interaction, whether molecular or thermodynamic in origin, is still controversial.

To date, much work has been accomplished on the gelling properties of the polysaccharides. The polysaccharide interactions in dilute solutions have been studied to a lesser extent. In dilute solutions, the individual polymer coils or rods are separate and free to move independently, and their intermolecular interactions are negligible. Thus, polymer–polymer interactions can be detected by the increase in solution viscosity and elasticity. The objective of this study was to investigate the effect of xanthan acyl substituents on the interactions between xanthan and guar gum in dilute aqueous solutions. An oscillatory capillary rheometer was used to determine dynamic viscoelastic properties for the polysaccharide solutions. Intrinsic viscosity and viscoelastic measurements were used to characterize the synergistic interaction between the polymers.

Materials and Methods

Materials

Xanthan gum and guar gum were purchased from Sigma (Sigma-Aldrich, St. Louis, Mo., U.S.A.).

Preparation of deacetylated xanthan

Deacetylation of xanthan was achieved by dissolving 0.2% (w/v) of native xanthan in deionized distilled water, and adding 0.025 M KOH and 0.1% (w/v) KCl for 2.5 h at room temperature under an atmosphere of nitrogen. The alkali solution was neutralized with 0.05 M HCl to pH 6.5. The solution was dialyzed against deionized distilled water for 3 d by using a dialyzing tube (Snakeskin TM Pleated Dialysis Tubing; Pierce, Rockford, Ill., U.S.A.), and the deacetylated xanthan was recovered by lyophilization (Sloneker and Jeanes 1962).

Stock solutions preparation

The stock solutions of deacetylated xanthan (0.1%, w/v), native xanthan (0.1%, w/v), and guar gum (0.2%, w/v) were prepared by thoroughly dispersing the required amount of gum in deionized distilled water. The gum solutions were continuously stirred with a magnetic stirrer for 3 h at ambient temperature and heated for 30 min at 90 °C in a water bath to completely hydrate the gums. Guar gum was centrifuged at $3500 \times g$ for 1 h to remove the insoluble

particles. The solutions were dialyzed against deionized distilled water for 3 d by using a dialyzing tube (Snakeskin TM Pleated Dialysis Tubing), with a molecular weight cutoff of 10 kDa. Stock solutions were refrigerated at 4 °C to minimize bacterial growth.

Preparation of mixed solutions of xanthan and guar gum

To study the interaction between the polysaccharides in the dilute domain, the deacetylated and native xanthan gum solutions were diluted with deionized distilled water to a final concentration of 0.025%, whereas the guar solution was diluted to 0.075%. The gums were blended at the following ratios: 100% xanthan:0% guar, 80% xanthan:20% guar, 60% xanthan:40% guar, 40% xanthan:60% guar, 20% xanthan:80% guar, and 0% xanthan:100% guar. The final concentrations of the mixtures were 0.025%, 0.035%, 0.045%, 0.055%, 0.065%, and 0.075%, respectively. Freshly prepared xanthan and guar solutions were mixed at 25 °C and stirred with a magnetic stirrer for 3 min. The concentration of xanthan and guar solutions was confirmed by the phenol-sulfuric method (Dubois and others 1956).

Determination of acetyl and pyruvate contents

The acetyl and pyruvate contents of native xanthan and deacetylated xanthan were determined by the hydroxamic acid (McComb and McCready 1957) and the 2,4-dinitrophenylhydrazine (Sloneker and Orentas 1962) methods, respectively.

Molecular weight determination of polysaccharides

The molecular weights of deacetylated xanthan, native xanthan, and guar gum were determined by high-performance size-exclusion chromatography (HPSEC), coupled on line with a multiangle laser light scattering detector (MALLS) and a refractive index detector. The MALLS detector was a DAWN DSP laser photometer from Wyatt Technology Corp. (Santa Barbara, Calif., U.S.A.) and the refractive index detector a Wyatt optilab DPS interferometric refractometer. A PL aquagel-OH mixed 8- μ m column (Polymer Labs, Amherst, Mass., U.S.A.) was used. A sample volume of 100 μ m/mL was injected at a flow rate of 1 mL/min using 100 mM NaCl as the mobile phase at a temperature of 30 °C. The dn/dc used for xanthan was 0.145 and for guar was 0.13. The data were analyzed by using Astra software version 4.5 (Wyatt Technology Corp.).

Determination of rheological measurements

The viscous (η') and elastic (η'') components of the polysaccharide solutions and their mixtures were measured as a function of oscillating shear rate by using an oscillating capillary rheometer (Viscoelasticity Analyzer, Vilastic 3; Vilastic Scientific Inc., Austin, Tex., U.S.A.). The instrument and theory of measurement are described elsewhere (Thurston 1960, 1976; Yaseen and others 2005). The Viscoelasticity Analyzer is based on the principles of generating oscillatory flow at a selected frequency within a straight, cylindrical stainless steel tube (0.0504 cm radius and 6.038 cm length). The Vilastic instrument produces an oscillatory flow in a capillary and measures the pressure and volumetric flow rate, allowing the determination of both viscous and elastic components of a fluid sample.

The complex coefficient of viscosity (η^*) consists of viscous (η') and elastic (η'') components, and is defined as:

$$\eta^* = \eta' - i\eta'' \quad (1)$$

where i is an imaginary number. The η' and η'' are related to dissipated and recovered energy, respectively. Similarly, complex rigidity

(G^*) is defined as:

$$G^* = G' + iG'' \quad (2)$$

where G' is the storage modulus and G'' is the loss modulus. The complex coefficient of viscosity is related to the complex rigidity modulus by

$$\eta^* = G^*/i\omega \quad (3)$$

or $\eta' = G'/\omega$ and $\eta'' = G''/\omega$, where the radian frequency $\omega = 2\pi f$, and f is the frequency in Hertz.

The η' and η'' of dilute solutions of xanthan and guar were determined in the shear-rate range 0.8 to 30 s^{-1} at a frequency of 2 Hz. Morris and Taylor (1982) reported that oral perception of solution viscosity correlated well with viscosity measurements at 10 s^{-1} . Thus, all η' and η'' calculations were determined at 10 s^{-1} . Rheological measurements were carried out at 20 ± 0.1 °C by using a temperature-controlled circulating water bath (Haake DC5; Gebr. Haake GmbH, Karlsruhe, Germany). The Viscoelasticity Analyzer was calibrated with deionized distilled water at 20 °C before the verification procedure to further ensure that the rheometer was accurately operating.

Intrinsic viscosity determination

Intrinsic viscosity, denoted as $[\eta]$, is a useful experimental parameter in the study of dilute solutions. Intrinsic viscosity is a measure of the hydrodynamic volume occupied by the individual polymer molecules in isolation (Richardson and Kasapis 1998). In dilute solutions, the polymer chains are separate, and the $[\eta]$ of a polymer in solution depends only on the dimensions of the polymer chain. Because $[\eta]$ indicates the hydrodynamic volume of the polymer molecule and is related to the molecular weight, it provides deep insights on the molecular characteristics of a biopolymer (Rao 1999).

One approach to determine the intrinsic viscosity is through extrapolation to infinite dilution, according to the Huggins (1942) empirical expression:

$$\frac{\eta_{sp}}{C} = [\eta] + k' [\eta]^2 C \quad (4)$$

where the specific viscosity (η_{sp}) = $(\eta - \eta_s)/\eta_s = \eta_{rel} - 1$, the relative viscosity (η_{rel}) = η/η_s , and η and η_s are the apparent viscosities of the solution and the solvent, respectively. The extrapolations to zero concentration are usually determined by plotting η_{sp}/C against C or $\ln(\eta_{rel})/C$ against C , which would result in straight lines, respectively. Tanglertpaibul and Rao (1987) determined the intrinsic viscosity from the relative viscosity by using the expression:

$$\eta_{rel} = 1 + [\eta] C \quad (5)$$

The $[\eta]$ was obtained from the slope of the η_{rel} against C plot, which gave straight lines, with linear regression correlation coefficients in the range 0.99 to 1.0. Chou and Kokini (1987) suggested a similar method for polyelectrolyte, in which the interactions between macromolecules in dilute solutions are not existent, and the second term of the Huggins equation is negligible; therefore, a plot of η_{sp} against C is linear.

In this study, the $[\eta]$ was determined for each solution by measuring relative viscosities of polysaccharide solutions within the range $1.2 < \eta_{rel} < 2.0$ at $\gamma = 10 \text{ s}^{-1}$. The intercept of the η_{sp}/C against C plot in the dilute region gave the first estimation of $[\eta]$ for guar gum,

whereas the slope of the η_{rel} against C plot gave the 1st estimation of $[\eta]$ for xanthan and xanthan–guar mixtures.

Statistical analysis

A 2-way factorial design was used for the study of rheological properties. For all polysaccharides samples, 3 replications and 2 subsamples were performed. The analysis of variance (ANOVA) and general linear models procedure (GLM) were conducted with SAS (2002–2003) (version 9.1; SAS Inst. Inc., Cary, N.C., U.S.A.). Comparisons among treatments were analyzed by using Fisher's least significant difference (LSD), with a significance level of $P < 0.05$.

Results and Discussion

Characterization of polysaccharides

Values of acetyl and pyruvate contents, and weight averaged molecular weights for the polysaccharides, are given in Table 1. The weight averaged molecular weights of native xanthan (2.65×10^6) and deacetylated xanthan (2.4×10^6) were much larger than that of guar gum (1.45×10^6). Some reduction in weight averaged molecular weight of native xanthan occurred due to the chemical modification. The acetate and pyruvate contents of native xanthan were 3.53% and 0.9%, respectively. Deacetylation of xanthan removed approximately 91% of the acetate content, but it did not affect the pyruvate content of xanthan.

Dynamics of polysaccharides interactions

Figure 1a, b and 2a, b show the changes in η' and η'' as a function of shear rate for native xanthan, deacetylated xanthan, guar, and their mixtures in water. Over the entire range of shear rates, both deacetylated xanthan and native xanthan exhibited a pseudoplastic behavior. For xanthan–guar mixtures, viscosity shear-rate dependence was observed for all mixtures, except for xanthan:guar at a ratio of 1:4. No shear-rate dependence was observed over the entire range of shear rates for guar gum. The guar behavior is consistent with viscosity results previously obtained for galactomannans over a larger range of shear rates ($10 < \gamma < 350 \text{ s}^{-1}$) (Bresolin and others 1997). No gels were formed for any of the xanthan–guar mixtures. For all shear rates studied, the η' of native xanthan and all native xanthan–guar mixtures was higher than the η'' , indicating liquid-like behavior in the dilute regime, whereas the η' of deacetylated xanthan and deacetylated xanthan–guar mixtures was lower than the η'' , except for deacetylated xanthan–guar mixture at ratio of 1:4, indicating gel-like behavior in the dilute regime. The η' and η'' values of polysaccharides at shear rate 10 s^{-1} are given in Table 2. Significant differences ($P < 0.05$) were found between the native xanthan–guar mixtures and deacetylated xanthan–guar mixtures. Deacetylated xanthan–guar mixtures exhibited significantly larger η' and η'' values than did native xanthan–guar mixtures.

The η_{rel} of deacetylated and native xanthan, guar, and their mixtures were plotted as a function of the mixing ratio in water, allowing the influence of deacetylation on the intermolecular interaction to be determined (Figure 3). The η_{rel} of deacetylated xanthan–guar

Table 1—Chemical composition of native xanthan, deacetylated xanthan, and guar gum

Polysaccharide	Acetate (%)	Pyruvate (%)	Weight averaged molecular weight
Native xanthan	3.51	0.9	2.65×10^6
Deacetylated xanthan	0.32	0.9	2.36×10^6
Guar	—	—	1.45×10^6

mixtures and native xanthan–guar mixtures differed with respect to the polysaccharide ratio, and the maximum synergy was observed at the ratio of 4:1. The relative viscosities of the polysaccharide mixtures were higher than the relative viscosities calculated for mixtures assuming no interaction, reflecting that intermolecular interaction occurred between xanthan and guar mixtures. These results are consistent with previous studies (Lopes and others 1992; Bresolin and others 1997) that showed viscosity of xanthan and guar blends in water was higher than the calculated value assuming no interaction for xanthan and guar mixtures, which supports the hypothesis of intermolecular interaction. The synergistic interaction in dilute aqueous solutions was further supported by elasticity measurements. Figure 4 shows the η' of deacetylated xanthan, native xanthan, guar, and their mixtures against polysaccharide ratio. In the mixtures with native xanthan, a small synergistic increase in η'' was observed, whereas the η'' synergistic interaction was significantly enhanced in the mixtures with deacetylated xanthan. The maximum synergistic interaction was noted at a xanthan:guar ratio of 4:1.

Our results demonstrated the influence of deacetylation on the increase of η' and η'' , which may reflect intermolecular binding between the polysaccharides. Tako and Nakamura (1985) and Smith

and others (1981) reported that acetate stabilizes the ordered conformation of xanthan, whereas pyruvate destabilizes the conformation (Holzwarth 1976) due to the increasing electrostatic repulsions between the side chains. Removing the hydrophobic acetyl group from the side chain of xanthan significantly enhanced the synergistic interaction with guar gum in dilute aqueous solutions. The η_{rel} of deacetylated xanthan–guar mixtures was much stronger than the relative viscosity of native xanthan–guar mixtures. Deacetylation of xanthan strongly enhanced the synergistic interaction, possibly due to destabilizing the helical structure of xanthan and increasing xanthan chain flexibility, thus facilitating the formation of heterotypic junctions with guar gum. In aqueous solutions, the structure of xanthan undergoes an order–disorder transition from helix to coil structure. This conformational transition depends on temperature, ionic strength of solutions, nature of electrolyte, pH, and acetyl and pyruvate constituent contents (Holzwarth 1976; Morris and others 1977; Baradossi and Brant 1982; Paoletti and others 1983; Norton and others 1984). Xanthan gum is in the disordered conformation in water at room temperature. Optical-rotation studies (Lecourtier and other 1986; Milas and Rinaudo 1986; Cheetham and Mashimba 1988, 1991) have confirmed that xanthan is in the disordered conformation in

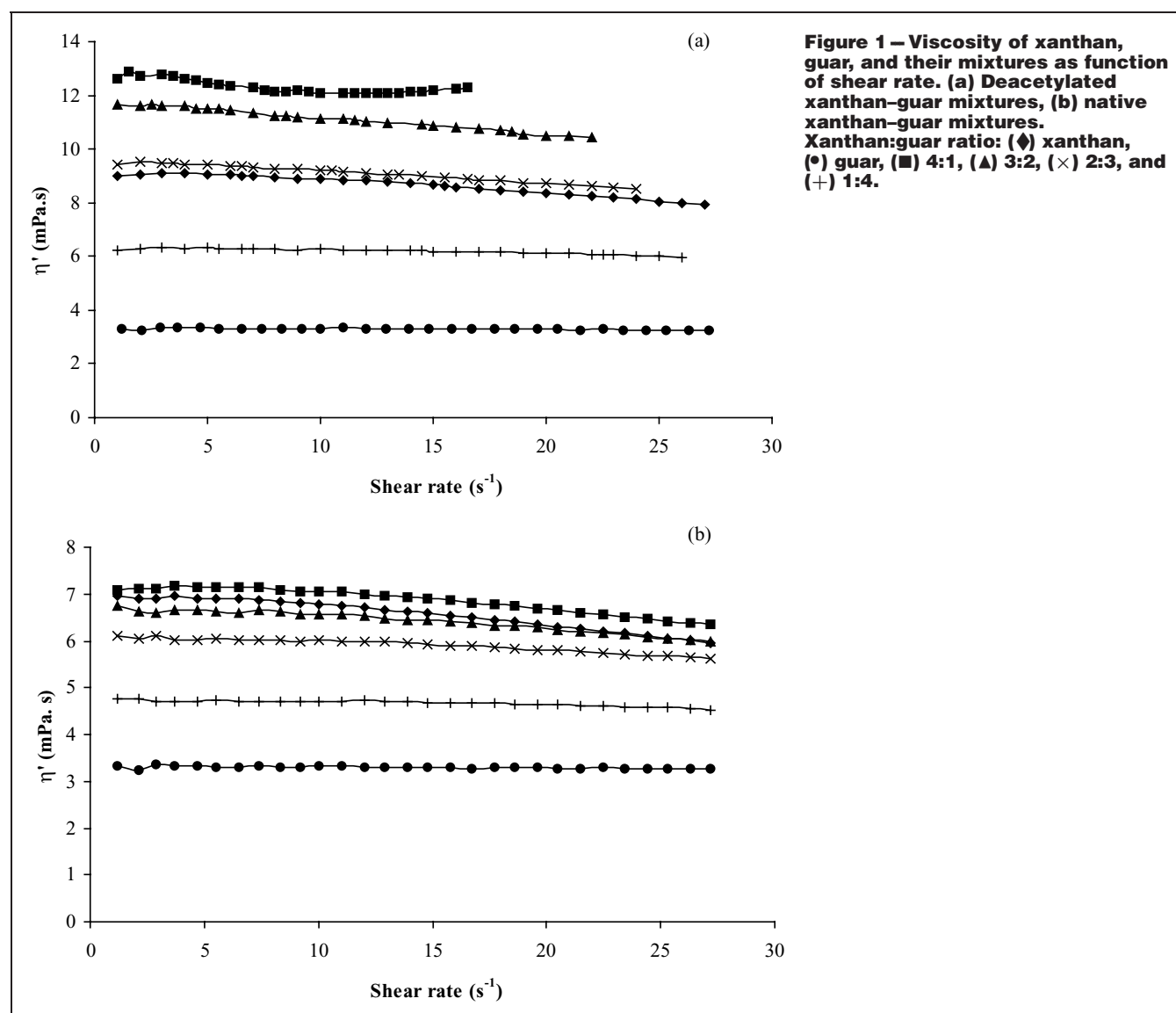


Figure 1 – Viscosity of xanthan, guar, and their mixtures as function of shear rate. (a) Deacetylated xanthan–guar mixtures, (b) native xanthan–guar mixtures. Xanthan:guar ratio: (♦) xanthan, (●) guar, (■) 4:1, (▲) 3:2, (×) 2:3, and (+) 1:4.

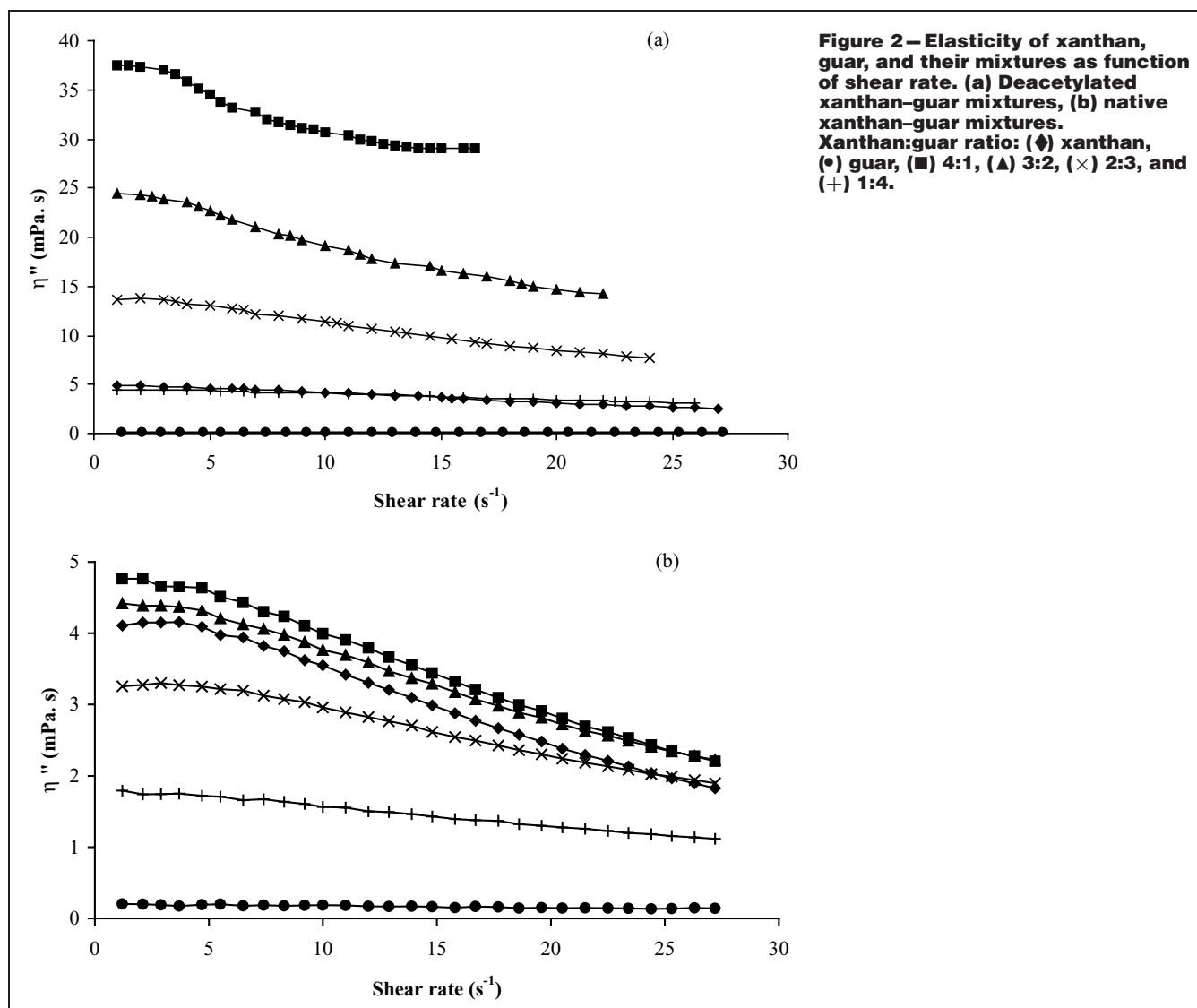


Figure 2—Elasticity of xanthan, guar, and their mixtures as function of shear rate. (a) Deacetylated xanthan–guar mixtures, (b) native xanthan–guar mixtures. Xanthan:guar ratio: (♦) xanthan, (●) guar, (■) 4:1, (▲) 3:2, (×) 2:3, and (+) 1:4.

water at room temperature. Electrostatic repulsions that involve glucuronate and pyruvate in the side chains are poorly shielded, thus favoring the disordered conformation (Cheetham and Mashimba 1991). Removing the acetyl groups of xanthan further disordered the structure of xanthan to a degree higher than that of native xanthan. Thus, the highly disordered xanthan was capable of directly interacting with guar to form heterotypic structures and a higher synergistic interaction. Because the synergistic interaction was stronger with the deacetylated xanthan, our results suggest that the degree of disordering of xanthan is critical in xanthan–guar interaction in water, which may explain the differences in the η' and η'' measurements between deacetylated xanthan–guar mixtures and native xanthan–guar mixtures. These results support previous studies (Cheetham and Mashimba 1988, 1991; Zhan and others 1993; Khouryieh and others 2006) in which intermolecular binding occurs between galactomannans and disordered segments of xanthan.

Intrinsic viscosities of polysaccharides

Intrinsic viscosity of polymers is dependent on their molecular weight and chain dimension (Flory 1953). In dilute solutions, the polymer chains are separate, so $[\eta]$ of a polymer in solution depends only on the dimensions of the polymer chain (Rao 1999). The intermolecular binding between xanthan and guar was further supported

Table 2—Effect of deacetylation on the viscosity (η') and elasticity (η'') parameters^c for native and deacetylated xanthan, guar, and their mixtures, measured at $\gamma = 10\ s^{-1}$

Xanthan:Guar(%)	η' (mP. s)		η'' (mP. s)	
	Native xanthan: guar	Deacetylated xanthan: guar	Native xanthan: guar	Deacetylated xanthan: guar
100:0	6.78 ^a ± 0.15	8.93 ^b ± 0.92	3.55 ^a ± 0.11	4.23 ^a ± 0.68
80:20	7.05 ^a ± 0.05	12.16 ^b ± 1.54	3.99 ^a ± 0.21	30.96 ^b ± 2.66
60:40	6.57 ^a ± 0.06	11.81 ^b ± 0.46	3.77 ^a ± 0.28	20.75 ^b ± 2.25
40:60	6.09 ^a ± 0.17	10.0 ^b ± 0.15	2.99 ^a ± 0.09	12.46 ^b ± 0.57
20:80	4.71 ^a ± 0.06	6.27 ^b ± 0.49	1.58 ^a ± 0.02	4.08 ^b ± 0.52
0:100	3.24 ^a ± 0.14	3.24 ^a ± 0.14	0.16 ^a ± 0.03	0.16 ^a ± 0.03

^{a,b} Means followed by the same letters in the same row for η' or η'' are not significantly different ($P < 0.05$).

^c Results are expressed as means ± SD for 3 replications.

by the intrinsic viscosities of xanthan and guar mixtures (Figure 5). The intrinsic viscosities of deacetylated xanthan–guar mixtures were higher than the calculated values assuming no interaction, whereas the intrinsic viscosities of native xanthan–guar mixtures were lower than the calculated values assuming no interaction, demonstrating that intermolecular binding may have occurred between xanthan and guar. These results are consistent with a previous study

conducted by Wang and others (2002), except that the intermolecular binding occurred between ordered xanthan and guar gum. The strong intermolecular binding between deacetylated xanthan and

guar can be attributed to the destabilized helical structure of xanthan and the increased chain flexibility. The intrinsic viscosities of native xanthan–guar mixtures decreased as the xanthan fraction decreased

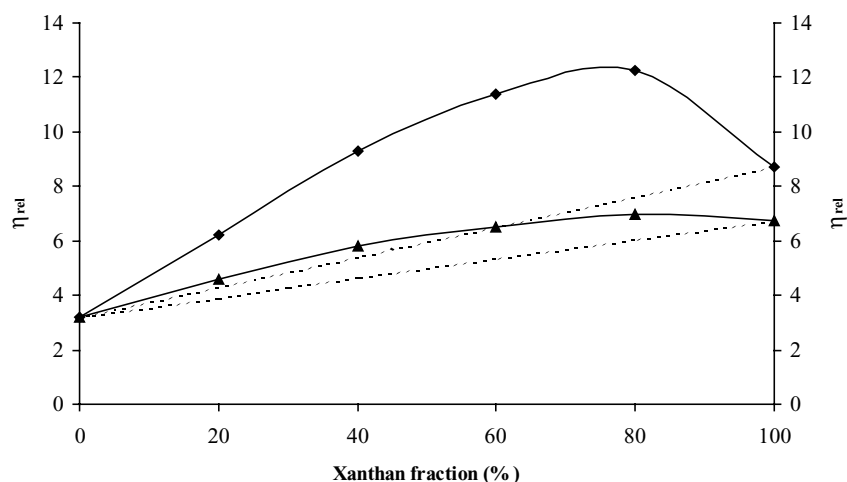


Figure 3 – Relative viscosity of xanthan, guar, and their mixtures. (♦) Deacetylated xanthan–guar mixtures; (Δ) native xanthan–guar mixtures; and (—) values calculated for mixtures assuming no interaction.

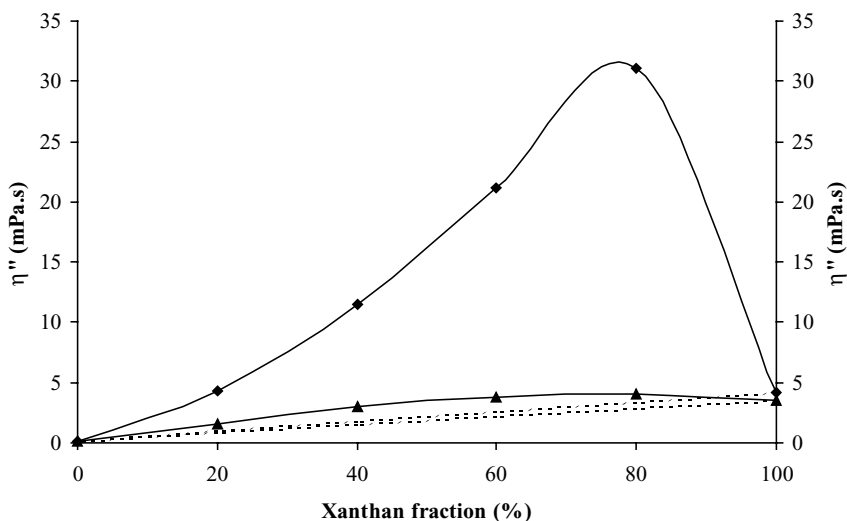


Figure 4 – Elasticity of xanthan, guar, and their mixtures. (♦) Deacetylated xanthan–guar mixtures; (Δ) native xanthan–guar mixtures; and (—) values calculated for mixtures assuming no interaction.

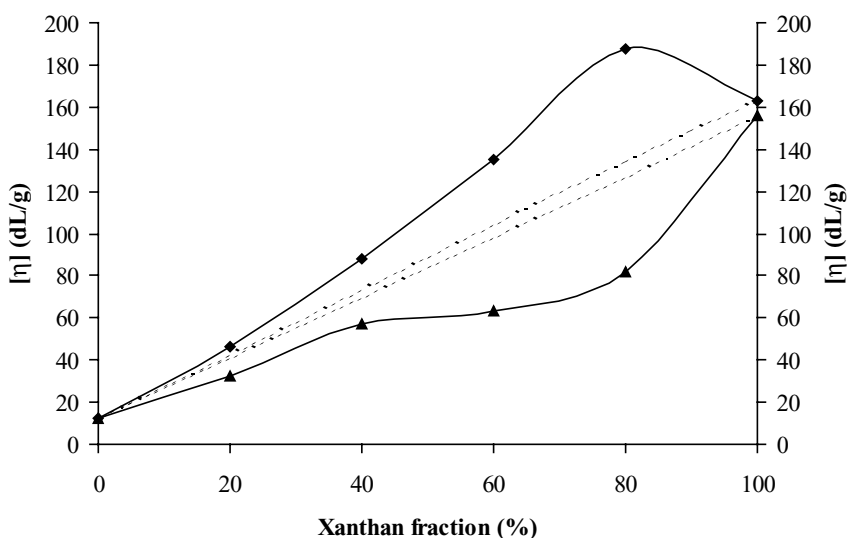


Figure 5 – Plots of intrinsic viscosities against xanthan fraction. (♦) Deacetylated xanthan–guar mixtures; (Δ) native xanthan–guar mixtures; and (—) intrinsic viscosity calculated from the weight averages of the 2 individuals, assuming no interaction.

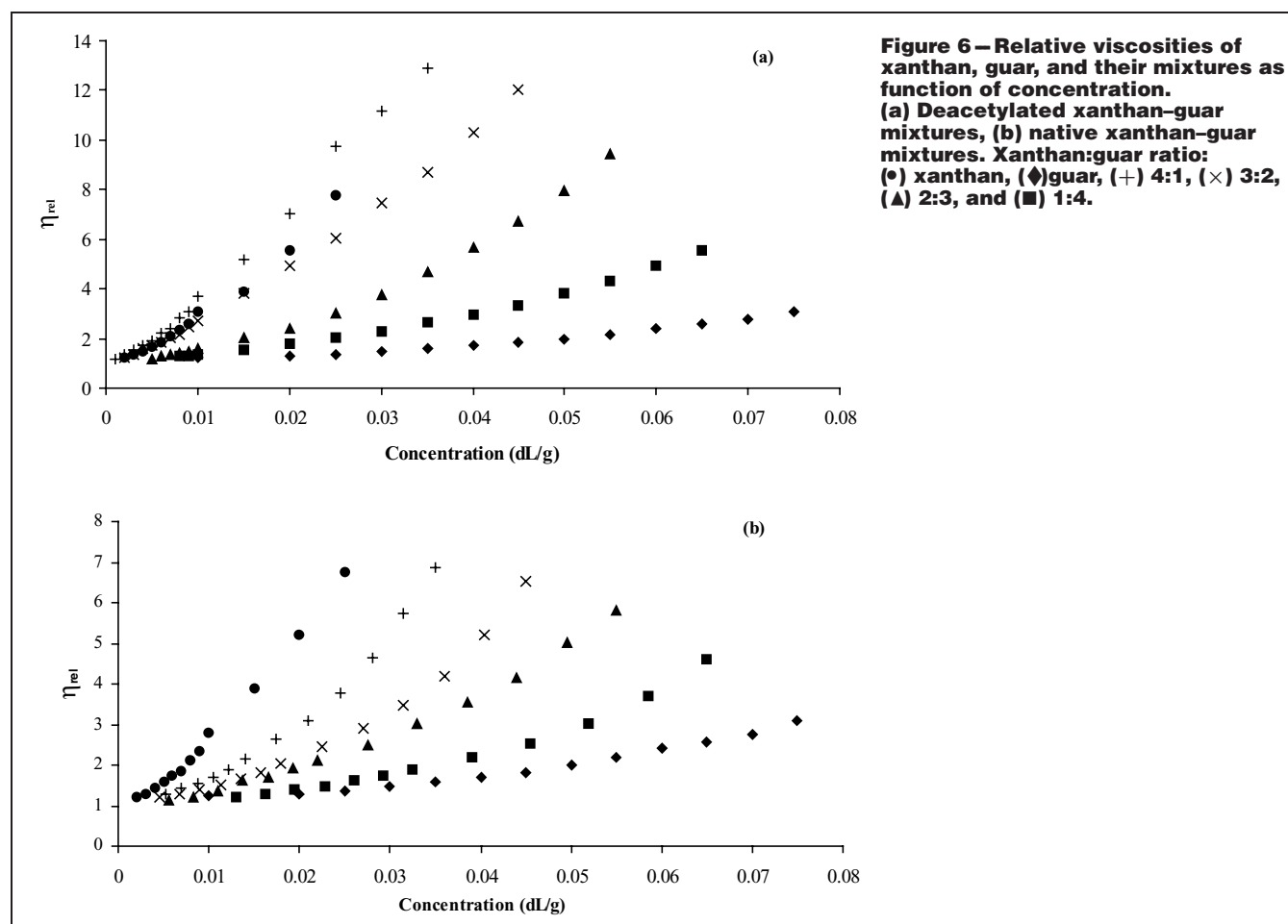
in the mixtures. The intrinsic viscosities of native xanthan–guar mixtures were lower than the calculated values assuming no interaction. Because xanthan plays a crucial role in controlling the viscosity of xanthan–guar mixtures, the dramatic decrease in the intrinsic viscosities of their mixtures may be attributed to the conformational change of xanthan from a helical form to a more flexible form due to binding of guar to xanthan. Xanthan conformation change outweighed the increase in intrinsic viscosity due to this binding; thus, the dramatic decrease in the intrinsic viscosities of the mixtures was observed.

The η_{rel} as a function of concentration for deacetylated xanthan, native xanthan, guar, and their mixtures is shown in Figure 6a and b. Straight-line relationships with large linear regression coefficients were obtained for xanthan and xanthan–guar mixtures in the η_{rel} range of 1.2 to 2. Similar results were found by Higiroy and others (2006). Native and deacetylated xanthan, and some of xanthan–guar mixtures, did not follow the Huggins equation at high dilution series, whereas the Huggins equation successfully fit the guar solutions. For a neutral polysaccharide such as guar the Huggins plot has the advantage of giving linear plots (Morris 1995). Plots of the reduced viscosity (η_{sp}/C) against the concentration of xanthan and some of the xanthan–guar mixtures resulted in a nonlinear relationship at low xanthan and low xanthan–guar mixture concentrations. Also, the Fuoss empirical equation (Fuoss and Strauss 1948) that was suggested for a flexible-chain polyelectrolyte did not show the typical viscosity–concentration relationship of flexible polyelectrolytes for xanthan alone. These findings were in agreement with Wang and

others (2002). Thus, this model was not successfully implemented to determine the intrinsic viscosity by extrapolation of experimental data, which prompted the use of the slope model (Tanglertpaibul and Rao 1987) to determine the $[\eta]$ by plotting relative viscosity against C (Eq. 5). Table 3 shows the values of the intrinsic viscosities of deacetylated xanthan, native xanthan, guar, and their mixtures. Xanthan and guar intrinsic viscosities were comparable to those reported by Launay and others (1984, 1997). The $[\eta]$ of deacetylated xanthan was higher than the $[\eta]$ of native xanthan. Deacetylated xanthan had a $[\eta]$ of 163 dL/g, whereas the $[\eta]$ of native xanthan was 154 dL/g, but the difference was not statistically significant ($P > 0.05$). This is consistent with work by Callet and others (1987), who reported that acetyl and pyruvate contents have no influence on the intrinsic viscosity of xanthan in dilute solution. The $[\eta]$ of guar gum was 12 dL/g. Deacetylated and native xanthan had a much higher $[\eta]$ than guar gum, which may be attributed to the significant difference in their chain stiffness. Xanthan may have a stronger chain stiffness than the flexible, random coil conformation of guar, which may lead to increase in its chain dimensions and thus a higher $[\eta]$.

Coil overlap parameter of polysaccharides

In dilute solutions, the individual polymer coils are separate from each other and are free to move independently. With increasing concentrations, the coils start to overlap and interpenetrate one another. The transition from dilute solutions to concentrated solutions is usually accompanied by a pronounced change in the concentration



dependence of solution viscosity (Morris and others 1981; Morris 1995). The corresponding concentration is called critical, or coil overlap, concentration (C^*). For random-coil polysaccharide solutions, except galactomannans, Morris and others (1981) reported

Table 3 – Effect of deacetylation on the intrinsic viscosity and slope^c of the double logarithmic plot of η_{sp} against $c[\eta]$ for native xanthan, deacetylated xanthan, guar, and their mixtures in the dilute domain

Xanthan: guar(%)	$[\eta]$ (dL/g)		Slope	
	Native xanthan: guar	Deacetylated xanthan: guar	Native xanthan: guar	Deacetylated xanthan: guar
100:0	155.7 ^a \pm 9.3	163.0 ^a \pm 5.0	1.38 ^a \pm 0.02	1.32 ^b \pm 0.05
80:20	82.2 ^a \pm 2.7	187.4 ^b \pm 5.8	1.50 ^a \pm 0.01	1.22 ^b \pm 0.03
60:40	63.1 ^a \pm 1.7	135.3 ^b \pm 5.9	1.44 ^a \pm 0.02	1.36 ^b \pm 0.06
40:60	56.9 ^a \pm 7.2	87.9 ^b \pm 7.3	1.55 ^a \pm 0.02	1.43 ^b \pm 0.07
20:80	32.8 ^a \pm 2.8	46.1 ^b \pm 2.8	1.68 ^a \pm 0.04	1.33 ^b \pm 0.02
0:100	12.0 ^a \pm 2.1	12.0 ^a \pm 2.1	1.44 ^a \pm 0.06	1.44 ^a \pm 0.06

^{a,b} Means followed by the same letters in the same row are not significantly different ($P < 0.05$).

^c Results are expressed as means \pm SD for 3 replications.

that the slope of double logarithmic plots of η_{sp} against $C[\eta]$ was close to 1.4 in a dilute regime, whereas in the concentrated regime the slope increased to 3.3. The C^* transition occurred at a value of $C[\eta]$ close to 4, and the η_{sp} at this degree of coil overlap was invariably close to 10. Guar gum was found to deviate from the above observations. The C^* transition occurred at a smaller value of the coil-overlap parameter, $C[\eta] = 2.5$, and the viscosity showed a higher dependence on concentration, with a slope of 5.1 instead of 3.3 (Morris and others 1981). In our study, all the polysaccharide systems were studied in dilute solutions. As shown in Figure 7a and b, no change in the slope of a double logarithmic plot of η_{sp} against the coil-overlap parameter ($C[\eta]$) occurred, indicating that no molecular entanglements were obtained and that xanthan (deacetylated and native), guar, and their mixtures were in the dilute domain. As shown in Table 3, the slope of a double logarithmic plot of η_{sp} against $C[\eta]$ for native xanthan and deacetylated xanthan was 1.38 and 1.32, respectively, and for guar was 1.44. Our results showed that the slopes of xanthan and guar were lower than those reported by Morris and others (1981), Cuvelier and Launay (1986), and Launay and others (1997), demonstrating that both xanthan (0.025%) and guar gum (0.075%) were

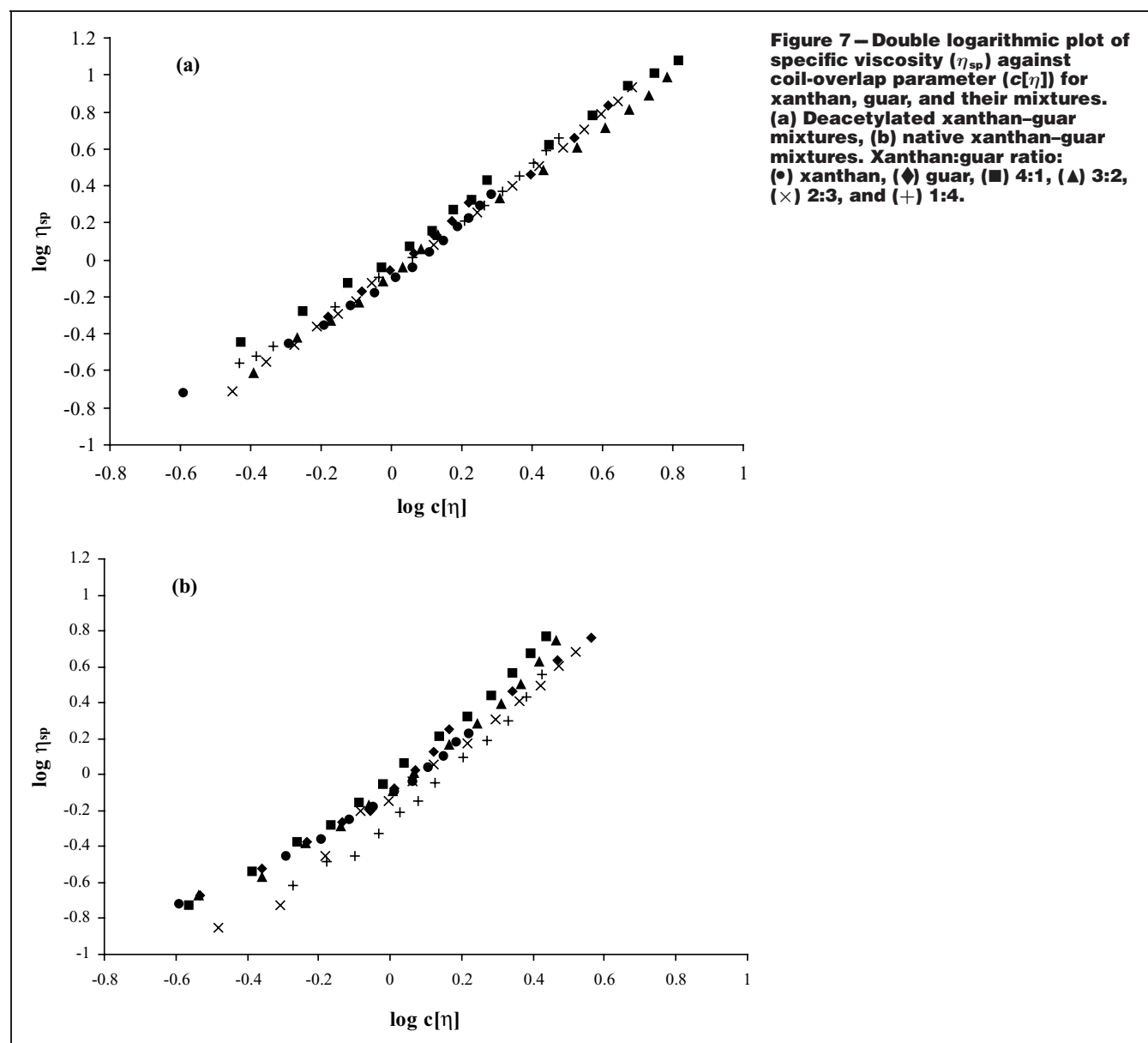


Figure 7 – Double logarithmic plot of specific viscosity (η_{sp}) against coil-overlap parameter ($c[\eta]$) for xanthan, guar, and their mixtures. (a) Deacetylated xanthan–guar mixtures, (b) native xanthan–guar mixtures. Xanthan:guar ratio: (●) xanthan, (◆) guar, (■) 4:1, (▲) 3:2, (×) 2:3, and (+) 1:4.

in the dilute domain ($C < C^*$). The slopes for deacetylated xanthan and deacetylated xanthan–guar mixtures were lower than those for native xanthan and native xanthan–guar mixtures, indicating more flexible xanthan due to the deacetylation.

Conclusions

Synergistic interactions for both native xanthan–guar mixtures and deacetylated xanthan–guar mixtures in the dilute aqueous solutions were observed. A much stronger synergistic interaction was noted for the deacetylated xanthan–guar mixtures. The η' of native xanthan and all native xanthan–guar mixtures was higher than the η'' , whereas the η' of deacetylated xanthan and deacetylated xanthan–guar mixtures was lower than the η'' . Deacetylated xanthan–guar mixtures exhibited significantly larger η' and η'' values than did native xanthan–guar mixtures. The intrinsic viscosities of deacetylated xanthan–guar mixtures were higher than the calculated values assuming no interaction, whereas the intrinsic viscosities of native xanthan–guar mixtures were lower than the calculated values assuming no interaction, demonstrating that intermolecular binding may have occurred between xanthan and guar. Destabilizing the helical structure of xanthan, due to deacetylation, played a significant role in its interaction with guar. Deacetylation of xanthan strongly enhanced the synergistic interaction with guar because it destabilized the helical structure and further disordered xanthan. Thus, the intermolecular binding occurred between the disordered segments of xanthan and guar gum in dilute aqueous solutions.

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